

**Development of a secondary organic aerosols formation mechanism and comparison with smog chamber experiments and atmospheric measurements**

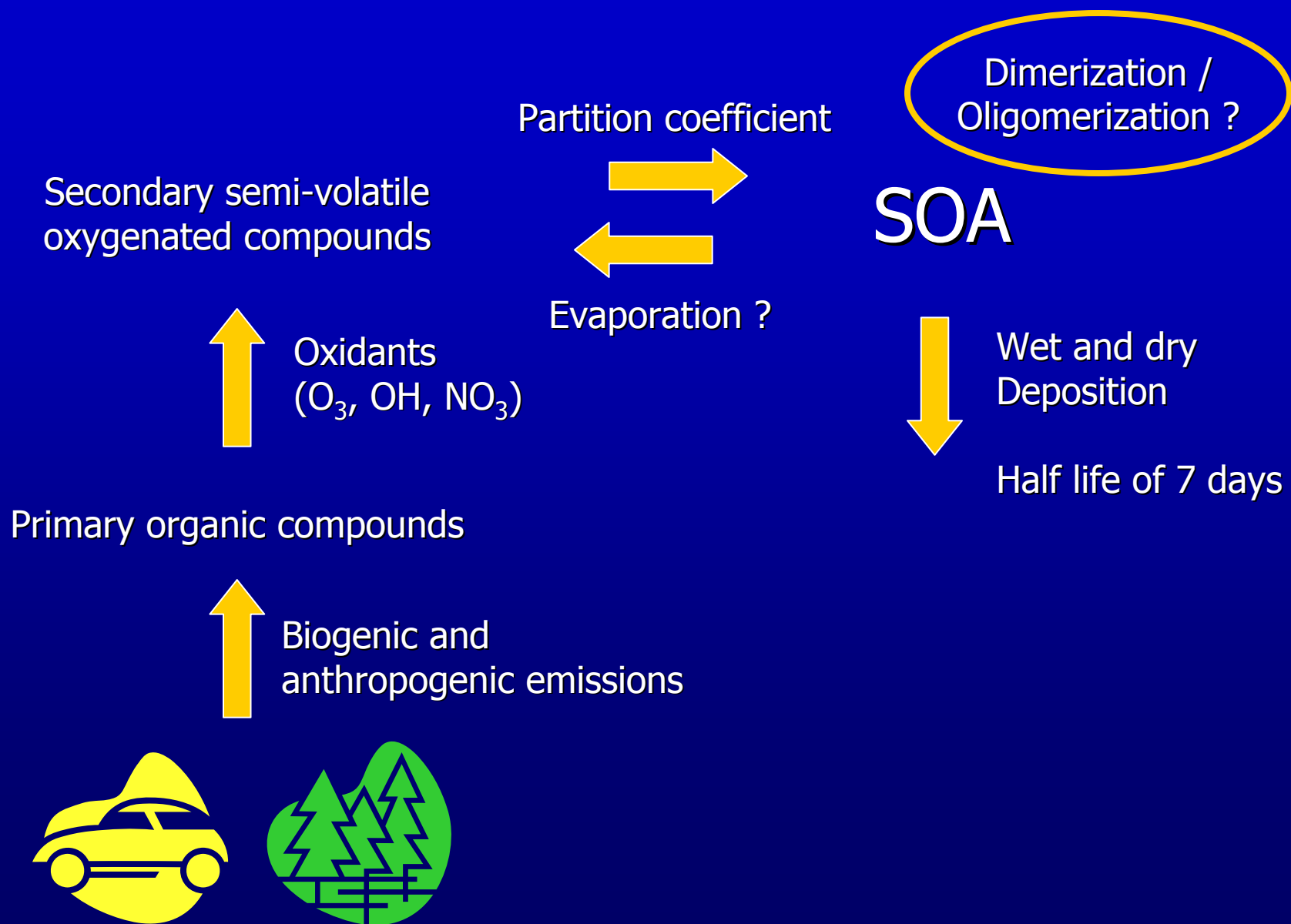
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# Introduction

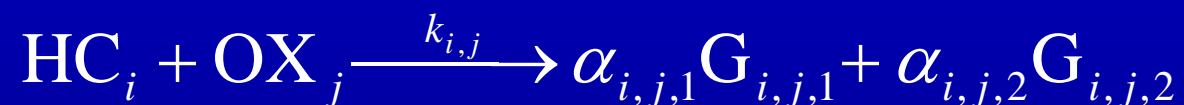
- ◇ Particulate matter (PM) plays a highly important role in the atmosphere. It exerts a strong influence on climate, modifying the amount of incoming radiation and changing the properties of clouds, and other indirect effects.
- ◇ Organic matter (OM) can contribute up to 90% of the total mass of PM, and a significant fraction of the OM are secondary organic aerosols (SOA), as high as 80% in polluted regions.
- ◇ Formation of SOA is poorly represented in current global chemical models, and this may be one of the main reasons why GCM models cannot properly reproduce aerosol field measurements.
- ◇ The yearly amount of SOA formed is almost unknown.

# SOA formation method



# SOA formation method

The “classic” method used to simulate the formation of SOA is a two-product modeling framework.



Typically,  $k_{i,j}$  and the stoichiometric coefficients  $\alpha_{i,j,k}$  are determined by fits to smog chamber experiments, and the chemical structure of the products  $\text{G}_{i,j,k}$  (that partition to the aerosol phase) remains unknown.

# SOA formation method

The chemical mechanism used includes 194 chemical species and 611 chemical reactions (Ito et al., JGR, 2006).

To partition to the SOA phase, a given secondary specie must have at least one of the following structural characteristics

- ◇ Be partially soluble.
- ◇ Be an aromatic acid.
- ◇ Be an aromatic compound with two functional groups that are not aldehydes.
- ◇ Have 12 or more carbon atoms.
- ◇ Have at least 10 carbon atoms and two functional groups.
- ◇ Have at least six carbon atoms and two functional groups, one of which is an acid.
- ◇ Be trifunctional.

# Relevant partitioning species

## Produced from anthropogenic VOCs

A-DI	Product of decomposition of carbonyl ( $\text{C}_6\text{H}_5\text{OH}(\text{OH})\text{CHO}$ )
ACHO	Benzaldehyde ( $\text{C}_6\text{H}_5\text{CHO}$ )
NITP	Benzyl nitrate ( $\text{C}_6\text{H}_5\text{ONO}_2$ )

## Produced from biogenic VOCs

IALD	Hydroxy carbonyl alkenes from isoprene ( $\text{HOCH}_2\text{C}(\text{CH}_3)=\text{CHCHO}$ )
INPN	Peroxide from terpenes + $\text{NO}_3$ ( $\text{NO}_2\text{OCH}_2\text{C}(\text{OOH})(\text{CH}_3)\text{CH}=\text{CH}_2$ )
ISNP	Peroxide from isoprene nitrate ( $\text{HOCH}_2\text{C}(\text{OOH})(\text{CH}_3)\text{CH}(\text{ONO}_2)\text{CH}_2\text{OH}$ )
ISNT	Isoprene nitrate ( $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}(\text{ONO}_2)\text{CH}_2\text{OH}$ )
MPAN	Peroxy methacryloyl nitrate ( $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OONO}_2$ )
MVK	Methylvinylketone ( $\text{CH}_2=\text{CHC}(\text{O})\text{CH}_3$ )
PINT	Acid from terpenes ( $\text{ONO}_2\text{C}_{10}\text{H}_{16}\text{OOH}$ )

# SOA formation method

$$[A_i]_{gas} = \frac{[A_i]_{aerosol}}{K_i M_0}$$

$$M_0 = [POA] + \sum_{i=1,n} [A_i]_{aerosol}$$

$[A_i]_{aerosol}$	concentration of the specie $A_i$ in the aerosol phase
$[A_i]_{gas}$	concentration of the specie $A_i$ in the gas phase
$K_i$	partition coefficient between the aerosol and gas phases
$M_0$	concentration of total organic aerosols
$[POA]$	concentration of primary organic aerosols
$n$	number of species that can partition to the aerosol phase

$$K_i = \frac{760 RT}{10^6 MW \zeta_i p_{L,i}^o}$$

$R$	ideal gas constant
$T$	temperature
$MW$	average molecular weight of the absorbing aerosol phase
$\zeta_i$	activity coefficient of the compound in the organic aerosol phase
$p_{L,i}^o$	compound vapor pressure (sub-cooled if necessary)

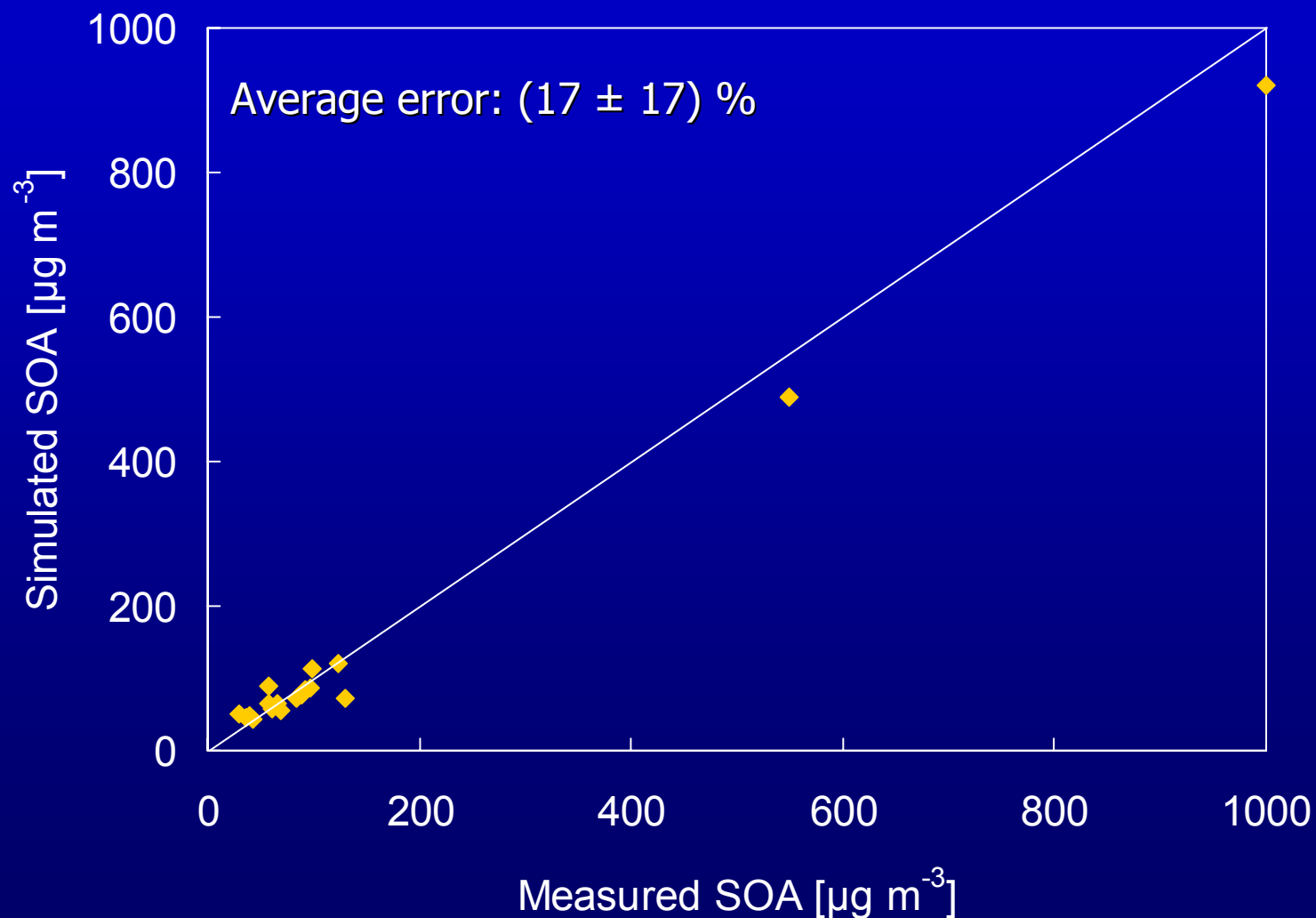
# Simulations

Several sets of experiments have been used to test the model

- ◇ Smog chamber measurements of SOA reported by Takekawa et al. (2003) and Kamens and Jaoui (2001) (xylene, toluene and  $\alpha$ -pinene).
- ◇ Ambient measurements of OA taken during the TORCH 2003 campaign (UK) under several meteorological conditions.
- ◇ Measurements and calculations from de Gouw et al. (2005) for the New England plume.
- ◇ Dependence of the SOA concentration on the VOC/NO<sub>x</sub> emissions ratio.

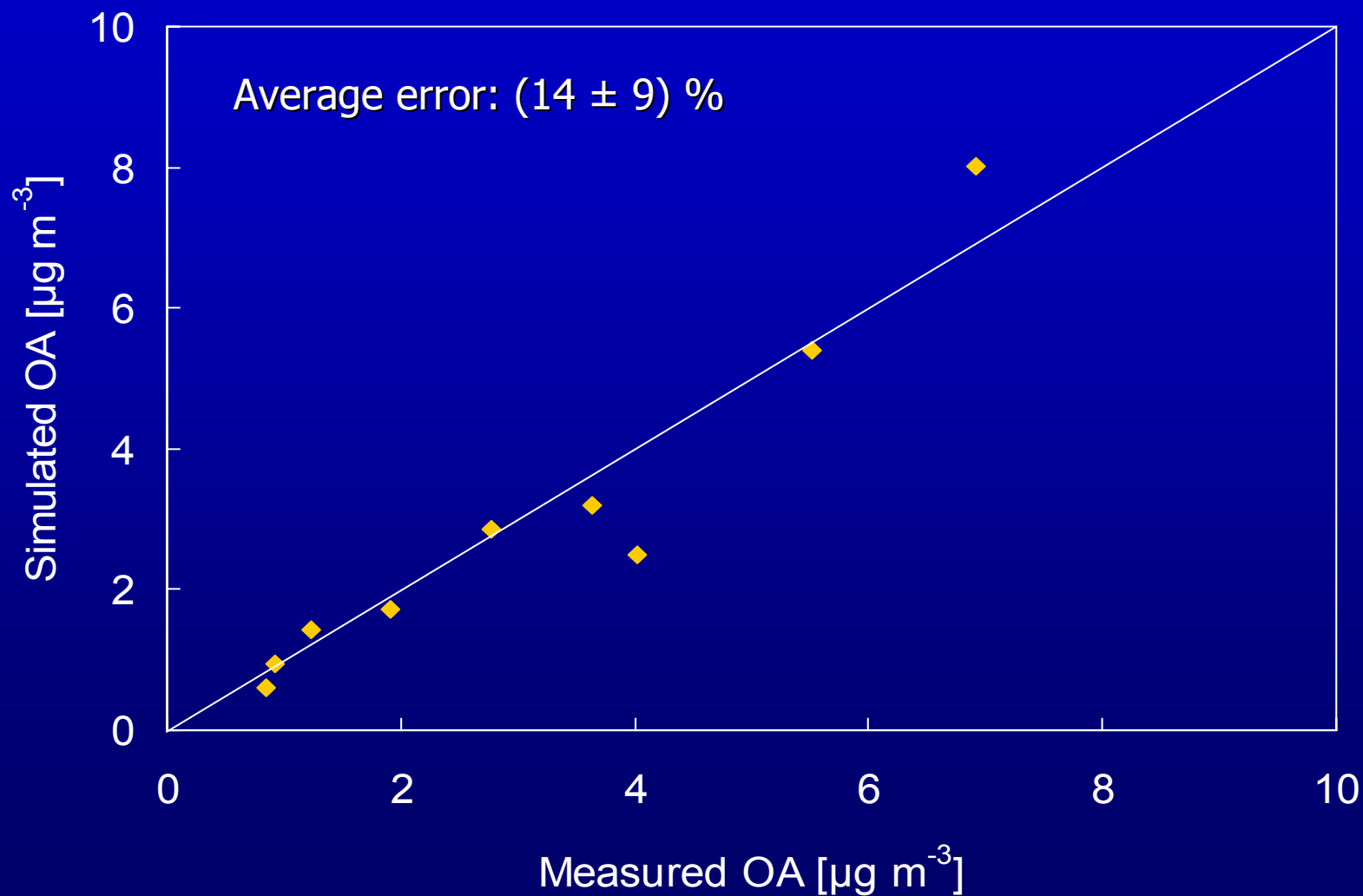


## Plot of simulated vs. measured SOA concentrations for several smog chamber experiments



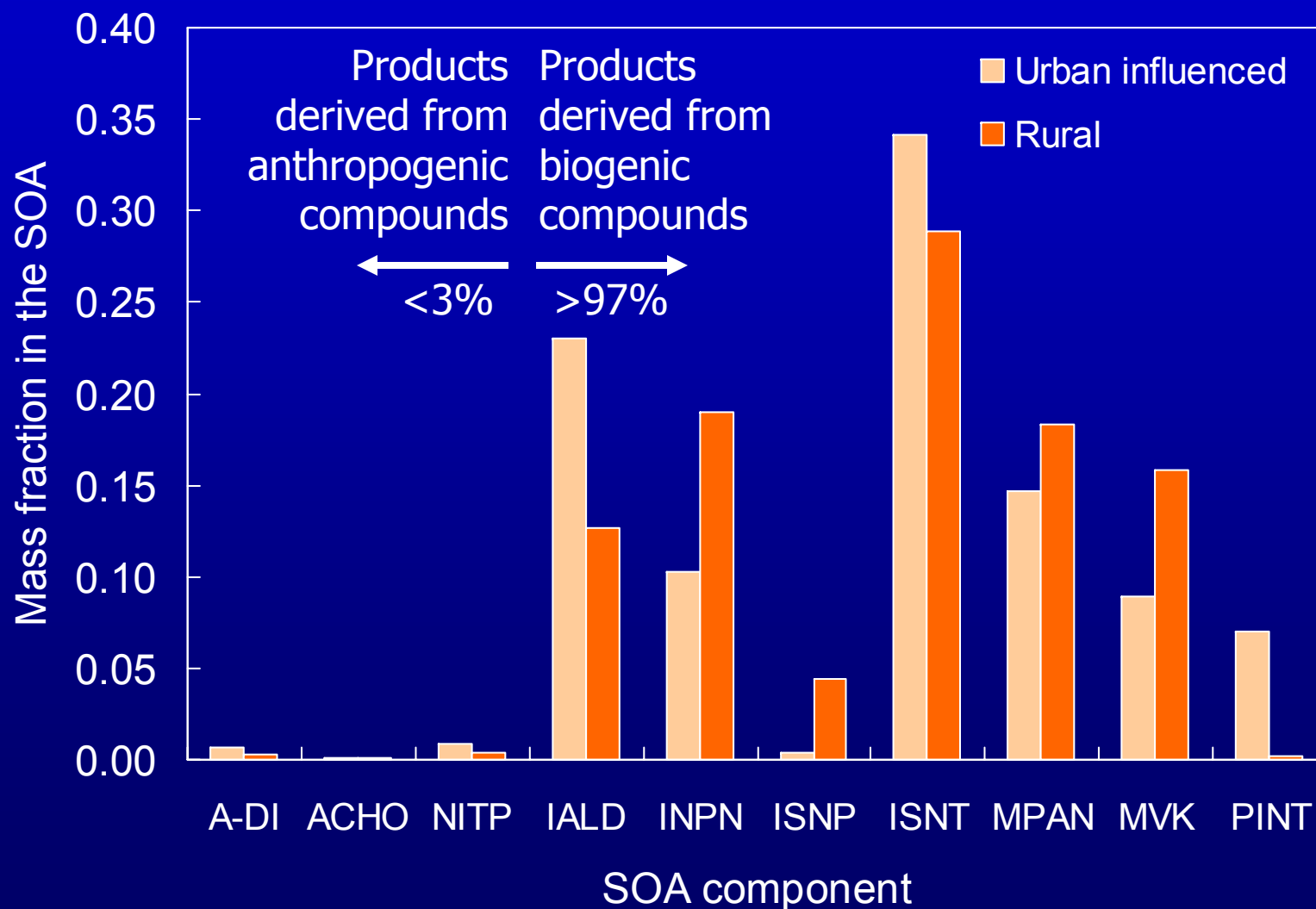
Exper. data: Takekawa et al., Atmos Env., 2003 - Kamens and Jaoui, Environ. Sci. Technol., 2001

# Plot of simulated vs. measured OA concentrations for the TORCH 2003 campaign

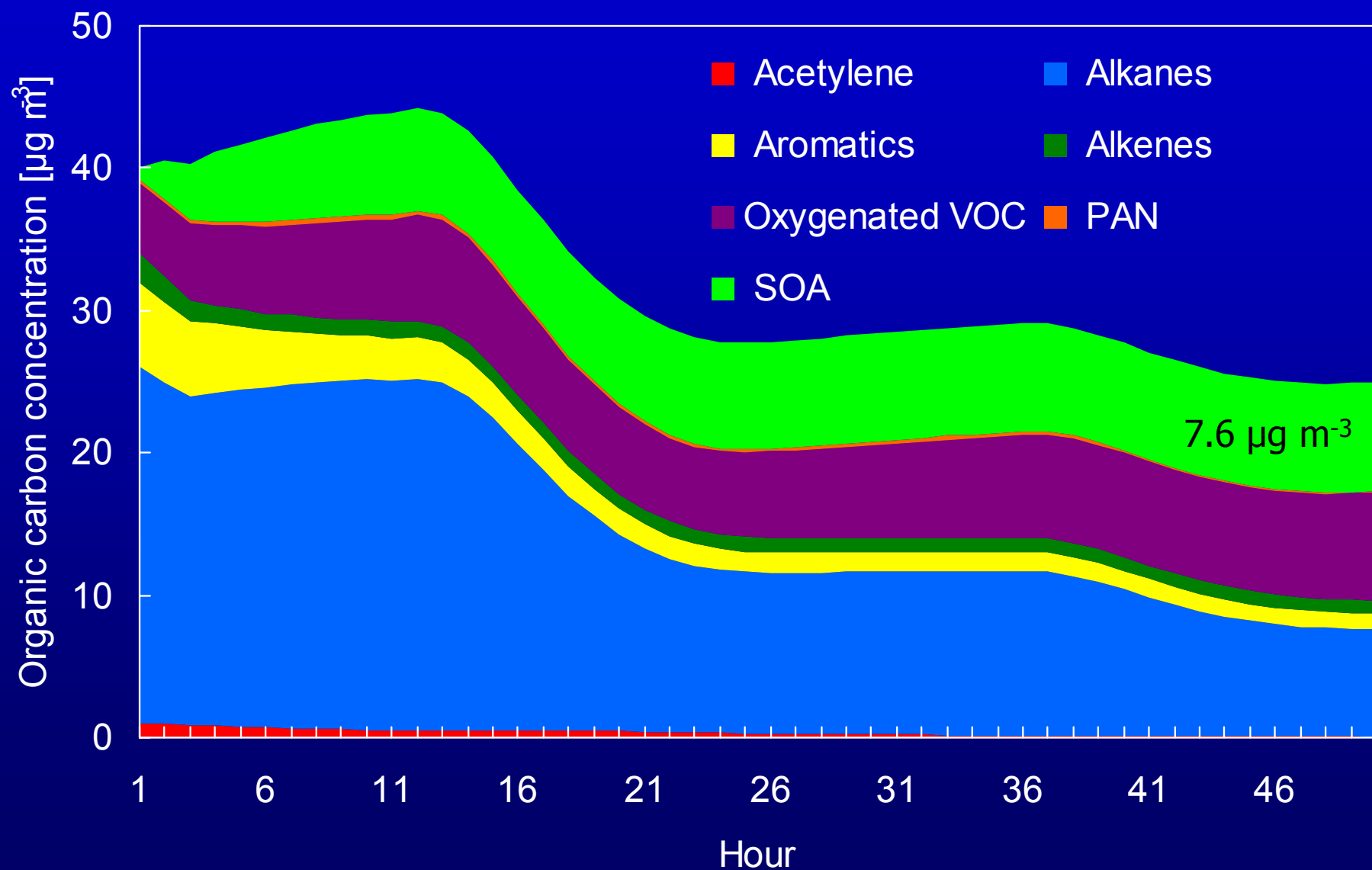


Exper. data: Johnson et al., ACP, 2006

## Species that partition to SOA under urban influenced and rural conditions

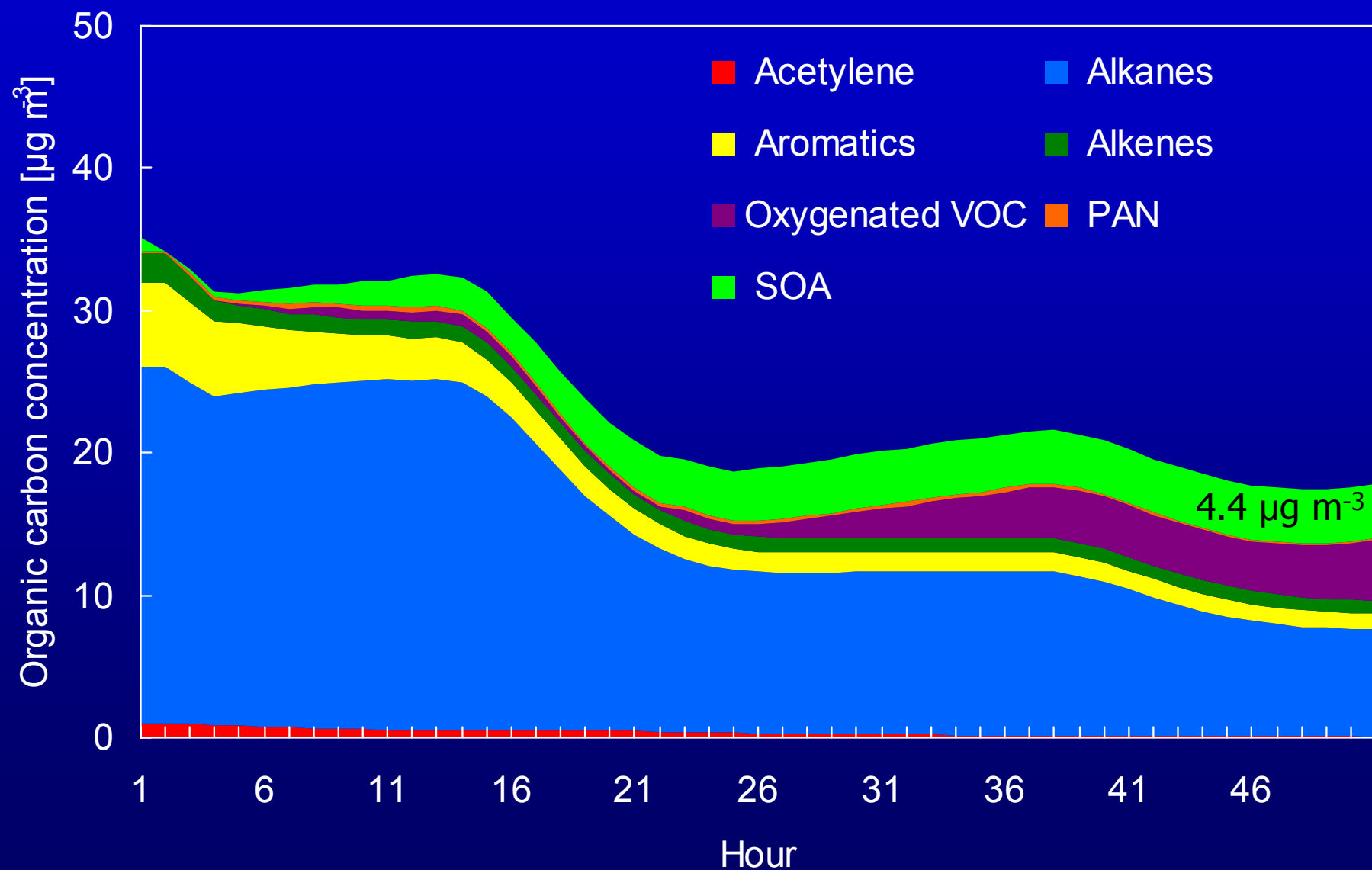


# Simulation of the anthropogenic New England plume

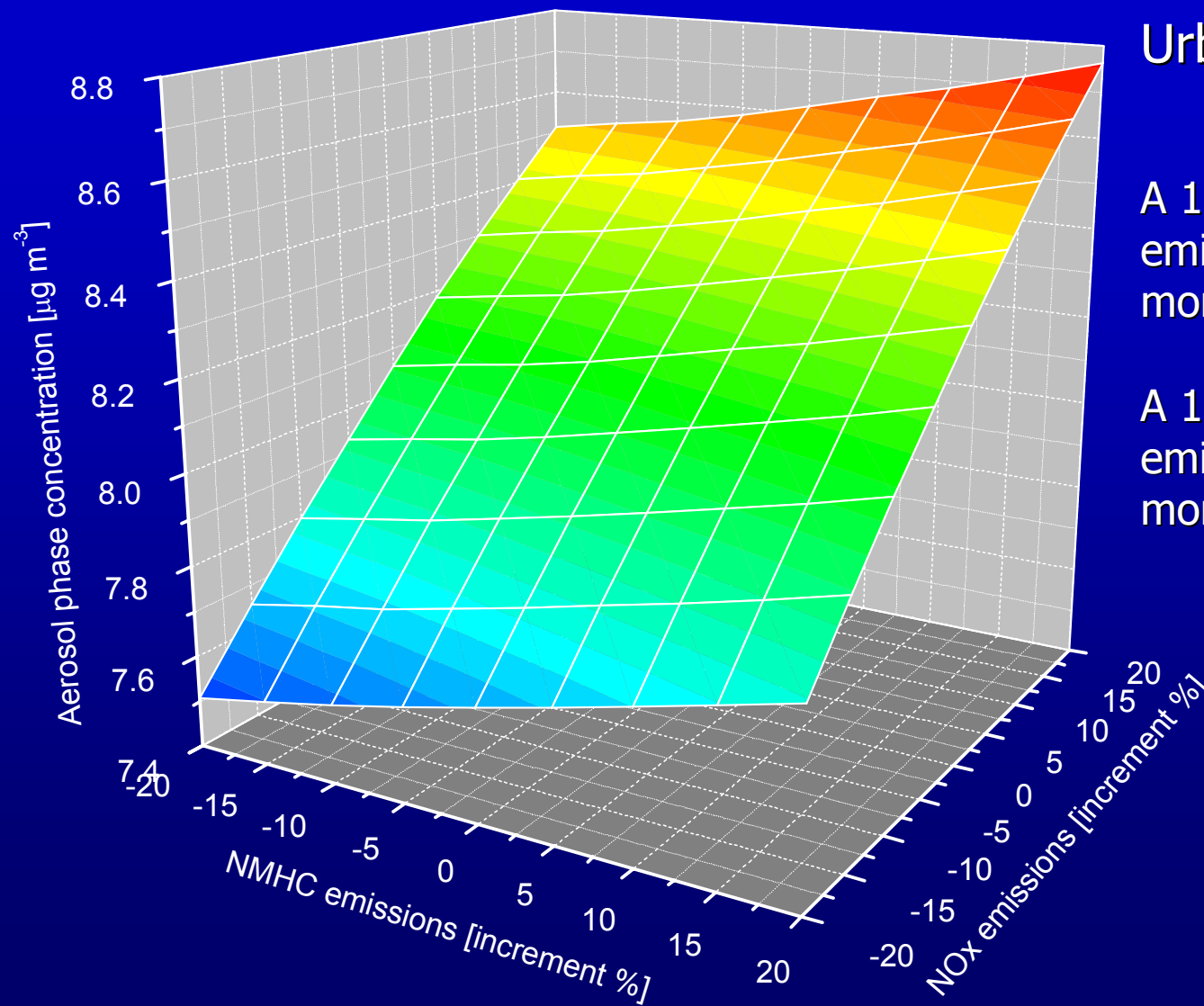


Exper. data: de Gouw et al., JGR, 2005

# Simulation of the New England plume without OVOC



## Variation on [SOA] depending on the VOC/NO<sub>x</sub> ratio

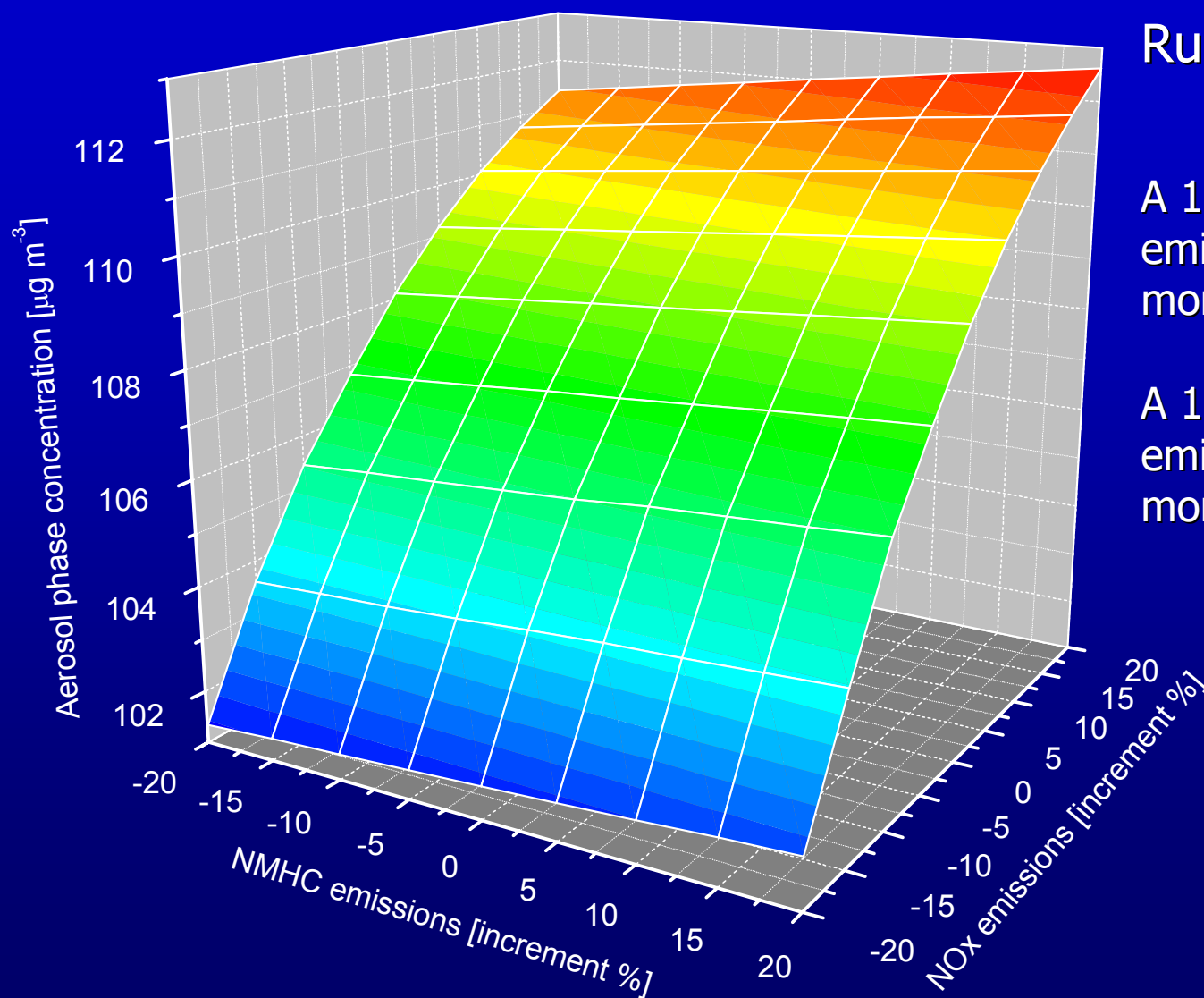


Urban influenced site

A 10% increase in NO<sub>x</sub> emissions produces 2% more SOA.

A 10% increase in VOC emissions produces <1% more SOA.

## Variation on [SOA] depending on the VOC/NO<sub>x</sub> ratio



Rural site

A 10% increase in NO<sub>x</sub> emissions produces 3% more SOA.

A 10% increase in VOC emissions produces <1% more SOA.

# Conclusions

- ◇ The model provides a reasonable replication of SOA formation for smog chamber measurements and the TORCH 2003 campaign.
- ◇ The choice of the compounds that can partition to the aerosol phase seems reasonable, since experimental values have been reproduced.
- ◇ The main advantage of this model, compared to other representations of SOA formation, is that the partitioning and stoichiometric coefficients are not fitted to experimental data, but calculated, making the model more flexible and able to include new compounds, to use new chemical mechanisms and to simulate the chemistry inside the aerosol phase.
- ◇ In rural and urban-influenced conditions, secondary organic products derived from biogenic emissions are responsible for most of the mass of the secondary organic aerosols. This fact is in agreement with previous modeling results.



## Future work

- ◇ An SOA formation module will be incorporated in the IMPACT 3-D global chemical transport model.
- ◇ Development of a complete wet and dry removal process for SOA, based on the removal processes for aerosols in the global aerosol model.
- ◇ Addition of reactions in the aerosol and heterogeneous phase, such as dimerization and polymerization to simulate the process of aerosol aging.